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THERMAL ENERGY STORAGE

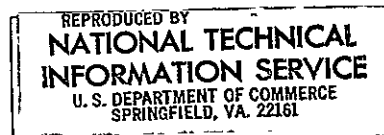INTERIM REPORT

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FOREWORD

This report presents a summary of the work accomplished to date on Contract NAS8-31100, "Thermal Energy Storage Development Study." Ms. B. Facemire of the George C. Marshall Space Flight Center is the contract monitor.

The general scope of the study is indicated as follows:

- Survey and review possible concepts for storing thermal energy.

- Evaluate the potentials of the surveyed concepts for practical applications in the low-and-high-temperature thermal control and storage, with particular emphasis on the low-temperature regime, and designate the most promising concept(s).

- Determine nature of further studies required to expeditiously convert the most promising concept(s) to practical applications.

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SUMMARY AND CONCLUSIONS

The principles involved in thermal energy storage by sensible heat, chemical potential energy, and latent heat of fusion are examined for the purpose of evolving selection criteria for material candidates in the low ($< 0^{\circ}$C) and high ($> 100^{\circ}$C) temperature ranges. The examination identifies some unresolved theoretical considerations and permits a preliminary formulation of an energy storage theory. A number of candidates in the low and high temperature ranges, located by literature search, are presented along with a rating of candidates or potential candidates. A few interesting candidates in the 0 to 100°C region are also included because of current interest in this range.

It is concluded that storage by means of reactions whose reversibility can be controlled either by product removal or by catalytic means appear to offer appreciable advantages over storage with reactions whose reversability cannot be controlled. Among such advantages might be listed higher heat storage capacities and more favorable options regarding temperatures of collection, storage, and delivery. Among the disadvantages are lower storage efficiencies.

candidates. Finally, some consideration is given to a general theoretical framework for HS/TC. These activities, of course, are very closely inter-related and are being conducted simultaneously. Results to date of the indi-cated activities are presented in the following sections. It might be well to emphasize that the work here reported is incomplete. Thus, the conclusions are tentative.

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Section 1
INTRODUCTION

Thermal storage and its complement thermal control or heat storage/ thermal control (HS/TC) for short, are technologies with applications in a number of areas. These technologies, however, are relatively undeveloped. Thus, although a few concepts are currently practical realities, numerous new concepts are possible. For example, heat storage by means of sensible heat, i.e., water and rock piles, and thermal control by means of latent heat of fusion and reflectance, i.e., phase change materials (PCMs) and paints, are well known. A seemingly multitude of new concepts, however, are presently being suggested because of the current energy crisis. To be able to judge which concept is most promising for a given application and thus deserving of further research and development would appear to be a formidable task at present because a general theoretical framework is generally lacking. Thus, each concept needs to be individually evaluated for any given application. Given the number of concepts currently appearing, one apparently could be busily occupied indefinitely and still not be sure one has chosen the best currently available concept for a given application.

The preceding situation generally applies to the applications here of interest — HC/TC at low and high temperatures with particular emphasis on long term storage of cryogens in space and low temperature thermal control in genera. Current technology in long-term cryogen storage relies primarily on dewar-type containers in conjunction with superinsulation (Ref. 1). The question of how to evaluate a multitude of old and new concepts for possible advantages over or in addition to insulated dewars is being handled in this study, given the current lack of a theoretical framework, by a three-fold approach. A number of concepts chosen on the rather subjective basis of experience and judgement are analyzed to elucidate the physical mechanisms and to identify thereby performance criterion. A search is then conducted of the literature for suitable

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search is then conducted of the literature for suitable candidates. Finally, some consideration is given to a general theoretical framework for HS/TC. These activities, of course, are very closely interrelated and are being conducted simultaneously. Results to date of the indicated activities are presented in the following sections. It might be well to emphasize that the work here reported is incomplete. Thus, the conclusions are tentative.

Section 2
PRINCIPLES OF POSSIBLE HS/TC MODES AND
THEIR OPERATION

A distinction is made between storage that essentially is reversible, i.e., heat is taken out as readily as it is put in (A type storage) and storage that involves some degree of irreversibility (B type storage). The following classifications accordingly are designated as A or B type

Generally heat storage in the solid or liquid phases is practically preferable to storage in the gaseous phases for the obvious reasons of less packing volumes and avoidance of pressure problems. In some situations, however, gases can be easily removed from the system for storage and readily added when needed. Water vapor is an excellent example. The following discussions, therefore, have not excluded systems involving gases.

2.1 A TYPE STORAGE

2.1.1 Sensible Heat

Sensible heat (or specific heat storage) is well known. In this storage mode input heat is stored as internal, molecular motions. It is fairly well known that the range of heat storage capacities or specific heats runs from about 0.4185 to 4.185 joules/gm-$^\circ$C. Water is remarkable in having one of the highest known heat capacities, $\sim$ 4.185 joules/gm-$^\circ$C.

An important consideration in sensible heat storage is the rate at which the system can store input heat as sensible heat. If the rate of heat input is faster than can be accommodated as sensible heat another heat storage mechanism, most often undesirable, comes into play. For example, consider the following schematic.
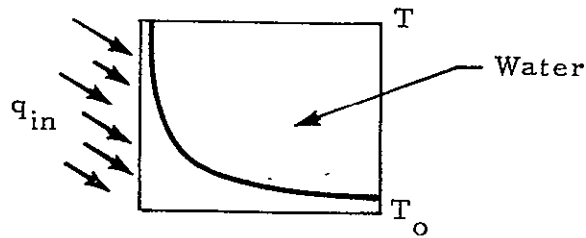
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Fig. 1 - Schematic of Transient Temperature Profile in Heat Storage by Sensible Heat

Obviously, if heat is input too fast, it cannot be transported fast enough within the system to hold local temperatures within acceptable limits. In such a case another, undesirable heat storage mechanism comes into play — boiling. It is even conceivable that boiling could occur at one end of the system while the other end was still at the initial temperature if the input heat rate were sufficiently high. The equation that describes the build up of temperature in a region is given by

$$\frac{dT}{dt} = \frac{k}{C_p \rho} \frac{\partial^2 T}{\partial x^2}$$

where the term $\frac{k}{C_p \rho}$ is the thermal diffusivity of the material. It is obvious, therefore, that a desirable characteristic for a sensible heat storage system would be a high thermal diffusivity. It can be seen, however, that high specific heats tend to make for low thermal diffusivity values. Thus for any given application care must be taken that the input heat flux does not exceed the ability of the system to respond appropriately.

An answer to the question of whether a material exists that has a substantially higher specific heat than about 4.185 joules/gm-$^\circ$C requires some delving into theory. It should be mentioned in this connection that second order phase transitions discussed in a following subsection may also be viewed as a sensible heat phenomenon. The present study has not gone into this aspect of specific heats thus far because of the feeling that the time probably would be better

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spent on some of the other concepts. Also not pursued thus far is the question of whether magnetic or electric fields could substantially increase specific heat. One applicable reference found in this area (Ref. 2) indicates that magnetizing a material has little effect on specific heats for ordinary conditions.
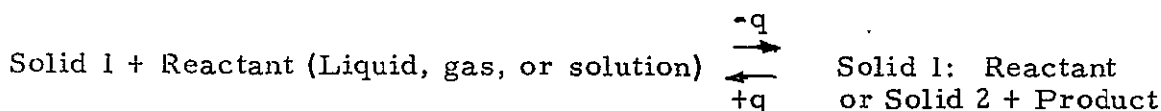
2.1.2 Reversible Chemical/Physical Reactions

It is well known that a chemical reaction has associated with it a heat, i.e.,

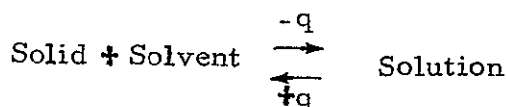$$A \underset{-q}{\overset{+q}{\rightleftharpoons}} B + C$$
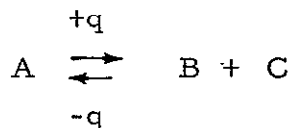
Dissociation of A absorbs q joules of heat, and recombination of the B and C liberates q joules of heat. For the moment we assume that the reaction involves only one phase (solid, liquid, or gas). The double arrows mean that the reaction occurs as readily in one direction as in the other, i.e., if a small amount of heat is added to the system the reaction goes one way, if a small amount of heat is subtracted, the reaction goes the other way. Such reactions have the effect of increasing the heat capacity of a system. In order for a chemical reaction to be effective as a storer of reversible heat, however, the rates of the forward and backward reactions must be sufficiently rapid to accommodate the input heat rate. Again, if the reaction rates are too slow, input heat will find another more accommodating, but probably undesirable, storage mode. Obviously, chemical reactions occurring within a solid phase will be generally slower than those occurring in the liquid or gas phases. In the solid phase mass transport is limited to diffusion which in the solid is quite a bit slower than in the liquid or gas phases ($D_{solid} \sim 10^{-10}$ cm^2/sec, $D_{liq} \sim 10^{-5}$ cm^2/sec, $D_{gas} \sim 10^{-1}$ cm^2/sec).

Most of what has been said about chemical reactions applies also to reversible chemical/physical reactions such as the following:

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$$\text{Solid 1 + Reactant (Liquid, gas, or solution)} \xrightleftharpoons[+q]{-q} \text{Solid 1: Reactant or Solid 2 + Product}$$

or

$$\text{Solid + Solvent} \xrightleftharpoons[+q]{-q} \text{Solution}$$

A distinction must be made, however, between chemical reactions involving only one degree of freedom and those involving two or more degrees of freedom. For example, in a reaction such as

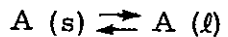$$N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)} \ ,$$
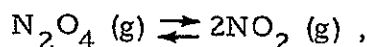
the equilibrium is a function of two variables. The number of variables upon which an equilibrium reaction depends is given by the well known Gibbs phase rule, i.e.,

$$\text{(Degrees of freedom)} = \text{(number of independent components)} - \text{(number of phases)} + 2$$

For the preceding reaction — one component, one phase — the degrees of freedom is two. Thus, if we vary temperature by adding heat, either the pressure of the system, if we keep the volume fixed, or the volume of the system, if we keep the pressure fixed, will change. On the other hand, a system such as

$$Ca (OH)_2 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + H_2O \text{ (g)}$$
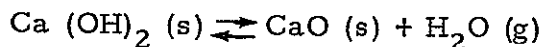
has three phases and two independent components. The degree of freedom, therefore, is one. Thus, we can change only one variable and still maintain equilibrium. If we change the amounts of CaO and H_2O by heat addition, the temperature and pressure will remain constant as long as three phases are present. It should be noted that phase change reactions, i.e.,

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$$A\ (s) \rightleftarrows A\ (\ell)$$
$$A\ (\ell) \rightleftarrows A\ (g)$$

also have one degree of freedom. Therefore, one degree of freedom reactions all behave similarly to the addition of heat — temperature and pressures remain constant during heat addition.

A reaction such as the following:

$$Pd - H\ \text{solid solution} \rightleftarrows H_2\ (g)$$
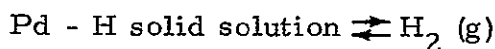
has two degrees of freedom (two components, two phases). An adsorption reaction of the following type, on the other hand, would appear to have one degree of freedom (two components and three phases):

$$\text{carbon (s)} + \text{carbon:adsorbed. } H_2\ (s) \rightleftarrows H_2\ (g)$$
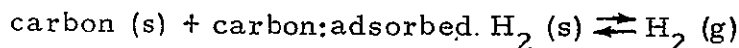
However, the phase carbon:adsorbed H_2 (s) is rather an ill-defined phase. Hydrogen molecules are undoubtedly moving around the carbon surface. Thus, just what is the carbon phase and what is the carbon:hydrogen phase is unclear. The author does not recall ever seeing a discussion of this point. Probably the degrees of freedom for a surface adsorption equilibrium are something like $1\frac{1}{2}$. In general the solid phase in reactions such as the preceding must be in a fine granular state to absorb or liberate a substantial proportion of the available thermal energy. Practical complications arising from settling, agglomeration, and heat transfer through the solid, granular phase, however, will probably be numerous.

2.1.3 Reversible Phase Change Reactions

These type of reactions can be broken down into three types: first order, second order, and "other type" phase transitions. First order phase transitions are characterized by the following derivatives being discontinuous.
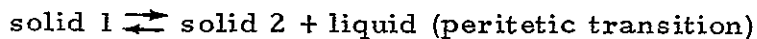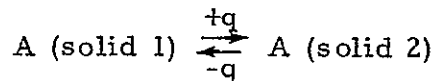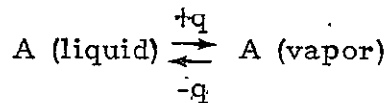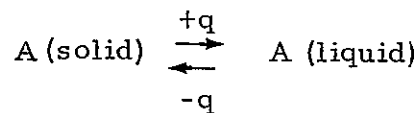
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$$\left(\frac{\partial G}{\partial t}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -V$$

where G is the Gibbs free energy. Second order phase transitions have continuous first derivatives of the Gibbs free energy, but discontinuous second derivatives, i.e.,

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

are discontinuous. First order phase transitions are exemplified by the following:

$$A \text{ (solid)} \underset{-q}{\overset{+q}{\rightleftarrows}} A \text{ (liquid)}$$

$$A \text{ (liquid)} \underset{-q}{\overset{+q}{\rightleftarrows}} A \text{ (vapor)}$$

$$A \text{ (solid 1)} \underset{-q}{\overset{+q}{\rightleftarrows}} A \text{ (solid 2)}$$

solid 1 $\rightleftarrows$ solid 2 + liquid (peritetic transition)

where q is the latent heat of phase change. The liquid/vapor transition is not usually considered for heat storage or thermal control because of the complications caused by vapor volume. The liquid/solid and solid/solid transitions occur at fixed, definite temperatures variously called melting points, freezing points, or transition points. The principles of solid/liquid phase transitions for HS/TC have been dealt with adequately previously (Refs. 3 through 7). Data on solid/solid phase transitions as heat storers will be found in Ref. 8.

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Second order phase transitions or order-disorder transitions involve a drastic change in heat capacity as a function of temperature, i.e., Fig. 2.
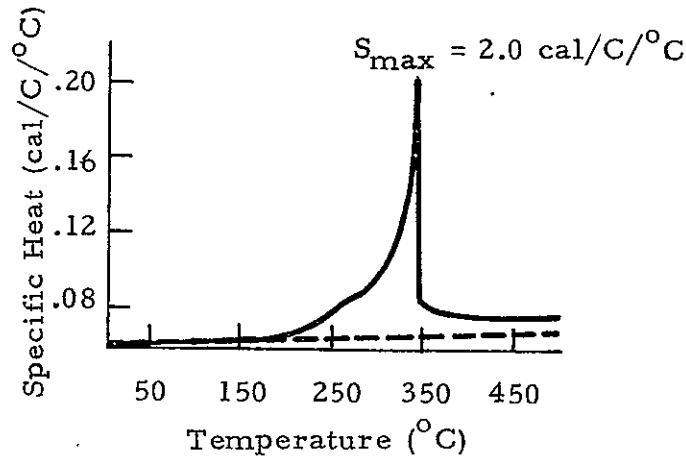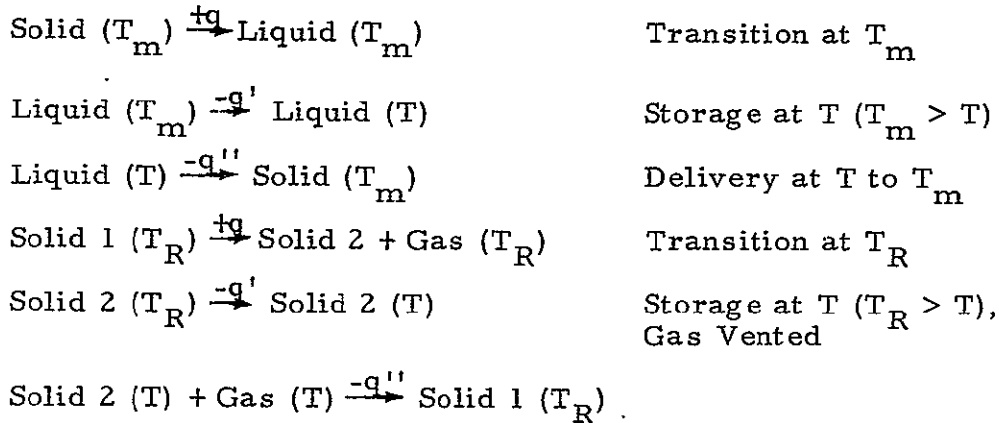

Fig. 2 - Variation of Specific Heat with Temperature of Cu_3Au Alloy

The discontinuity in specific heat is the result of an ordering-disordering of structure on cooling or heating. The onset of ordering appears at a definite, "critical" temperature called the Curie temperature. The ordering may have its origin in different molecules of a solid solution arranging themselves into a more ordered structure, or in magnetic or electric domain ordering. The latter two cases have not been investigated in this study as yet. The concept at first glance would not appear to have much potential for HC/TC because the spike is not very broad. Little additional heat, therefore, could be stored. Also, these type transitions are apparently quite slow. However, most of the data on these transitions come from studies of metallic alloys. There are indications that nonmetallic systems may possess more internal degrees of freedom than metal alloy systems and hence may display larger heat capacities because of transitions such as non-rotation ⟶ rotation. This area will be looked into a little further in the remainder of the study.
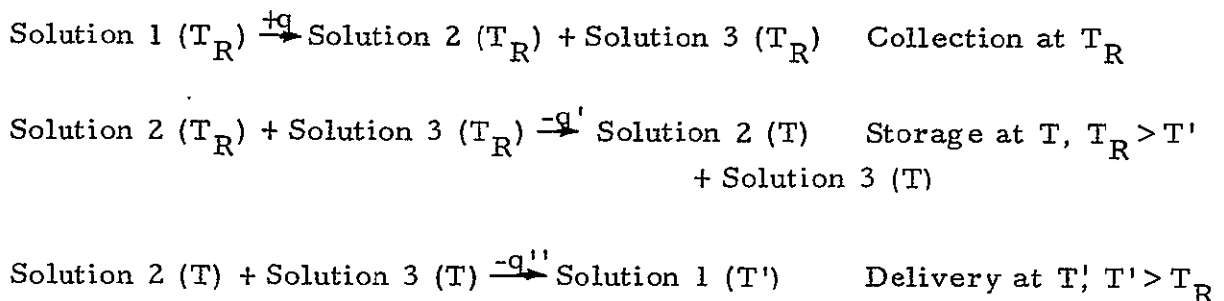
The "other type" phase transitions that would appear interesting for possible heat storage are the gel ⟶ liquid transitions. Very little has been found to date on these, but more information will be sought in the remainder of the study.

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2.2 B TYPE STORAGE

As indicated previously this type of heat storage involves some degree of irreversibility. In this type of storage some option exists over the temperatures of collection, storage, and delivery. To facilitate, discussion category B is broken down into two subcategories. Category B1 consists of situations where the collection and delivery reactions take place at essentially the equilibrium temperature, i.e., where $\Delta G \sim 0$. Thus, no work is done on or by the system during storage reaction. Any heat absorbed just increases the entropy of the system. Examples of such systems are as follows:

Solid (T_m) $\xrightarrow{+q}$ Liquid (T_m) Transition at T_m

Liquid (T_m) $\xrightarrow{-q'}$ Liquid (T) Storage at T $(T_m > T)$

Liquid (T) $\xrightarrow{-q''}$ Solid (T_m) Delivery at T to T_m

Solid 1 (T_R) $\xrightarrow{+q}$ Solid 2 + Gas (T_R) Transition at T_R

Solid 2 (T_R) $\xrightarrow{-q'}$ Solid 2 (T) Storage at T $(T_R > T)$, Gas Vented

Solid 2 (T) + Gas (T) $\xrightarrow{-q''}$ Solid 1 (T_R) .

In the above systems, collection and delivery are essentially at the equilibrium temperatures. The option exists, however, of storage at temperatures below the collection or delivery. In the B2 category, a part of the heat input goes into work performance. A B2 system is typified by the following sets of reactions:

Solution 1 (T_R) $\xrightarrow{+q}$ Solution 2 (T_R) + Solution 3 (T_R) Collection at T_R

Solution 2 (T_R) + Solution 3 (T_R) $\xrightarrow{-q'}$ Solution 2 (T) Storage at T, $T_R > T'$
+ Solution 3 (T)

Solution 2 (T) + Solution 3 (T) $\xrightarrow{-q''}$ Solution 1 (T') Delivery at T, $T' > T_R$

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In the preceding reactions some of the heat is converted to separative work. Thus, it would appear to be possible, by controlling the solution amounts, rates of mixing, and rates of heat withdrawal to deliver heat at a higher temperature than the collection temperature. The amount of heat delivered at the higher temperatures would, of course, be smaller than the amount collected at the lower temperature. The thermodynamics of the preceding category are not yet fully understood. Section 4, however, outlines progress to date on this aspect of the study. It would appear, however, that B2 type storage requires reactions possessing more than one freedom degree.

The transformation of heat into work other than chemical work has not been considered thus far. In the remainder of the study some consideration will be given to transformation of electrical energy into chemical work. It is felt at the moment that B type storage modes other than chemical, i.e., gravitational, surface, magnetic, elastic, etc., probably do not offer much potential for HS/TC.

In the following subsections some possible B1 and B2 storage modes are considered in more detail.

2.2.1 Irreversible Chemical/Physical Reactions

A chemical/physical reaction may be irreversible, i.e.,

$$A \xrightarrow[\text{(No backward reaction)}]{+q} B + C$$
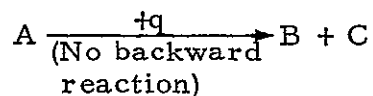
for one of three reasons: (1) one of the products is made unavailable for the backward reaction; (2) a high activation energy barrier exists to the backward reaction; or (3) so many additional reactions can occur between B and C that the chance of ever producing appreciable amounts of A from B and C is for all practical purposes nil. Case (3) obviously is of no further interest to us. Cases (1) and (2), however, are of high interest because of the possibility of heat storage as chemical energy. Such storage could occur at low or medium temperatures obviating the need for insulation. When wanted, stored heat could be liberated

by allowing B and C to recombine. Furthermore, by controlling the rate of the reaction, some control over the temperature of heat delivery also would be possible. Case (1) requires some ingenuity in system design, and case (2) an appropriate catalyst which, however, might not be so easy to identify. A couple of arrangements for preventing recombination of products are shown in Figs. 3, 4, and 5.
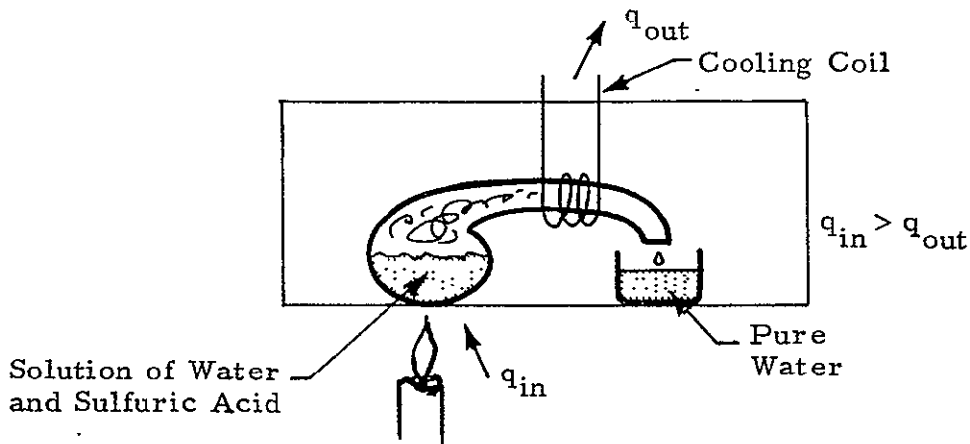

Fig. 3 - Example of B Type Storage Utilizing Separation of Reactants
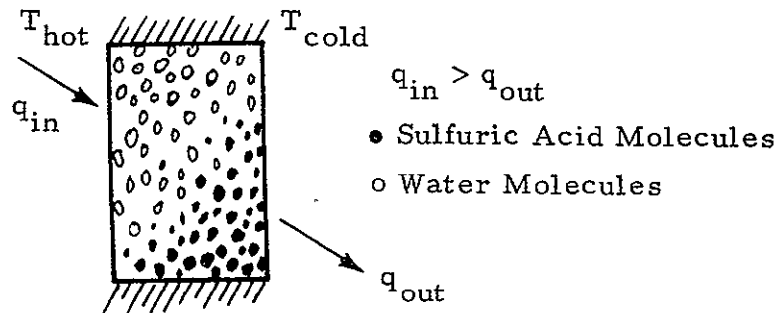

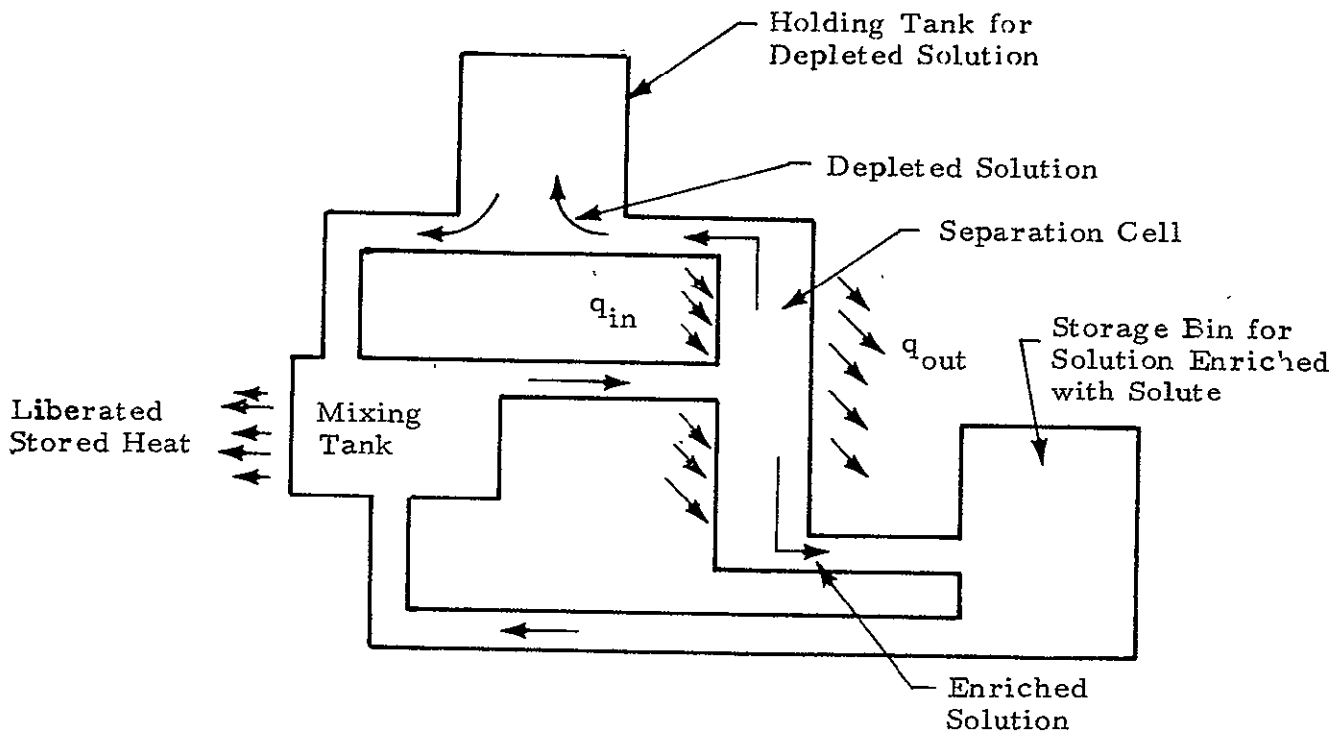Fig. 4 - Schematic of B Type Storage by Thermal Diffusion

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Fig. 5 .- Schematic of an HS/TC Device Based on Thermal Diffusion

In the preceding examples the stored heat could be liberated at will by remixing the pure water and the concentrated sulfuric acid.

In the preceding arrangements, passage of heat effects a separation of solution components. The responsible mechanism in Figs. 4 and 5 is a combination of thermal diffusion and convection. The separating effects of a temperature gradient on a solution is known either as thermal diffusion if the separation occurs within a gas phase or Soret effect if the separation occurs within the liquid phase. In an arrangement such as shown in Fig. 4 ordinary diffusion would remix the separated solution components if the heat flux were stopped. In Fig. 5, however, the products are separated to prevent remixing until desired.

The topic of separations by thermal diffusion or Clusius Dickel separations is too complicated to be gone into here. The operation of Clusius-Dickel separation cells has been dealt with extensively in a recent report (Ref. 10).

2.2.2 Irreversible Phase Changes

It is well known that a number of substances melt readily but exhibit resistance to freezing. In many cases, melts can be cooled far below their freezing temperatures with no freezing occurring. If, however, an appropriate seed or catalyst is introduced into the system crystallization proceeds with extreme rapidity, or until enough heat is liberated by the crystallization to monitor the rate of crystallization. Conceivably a scheme whereby a supercooled melt is flowed into a crystallizing chamber at an appropriate rate would give control over the rate of heat liberation, i.e., Fig. 6. Refs. 3 through 6 are as relevant to this concept as they are to the previously discussed reversible phase change concept.
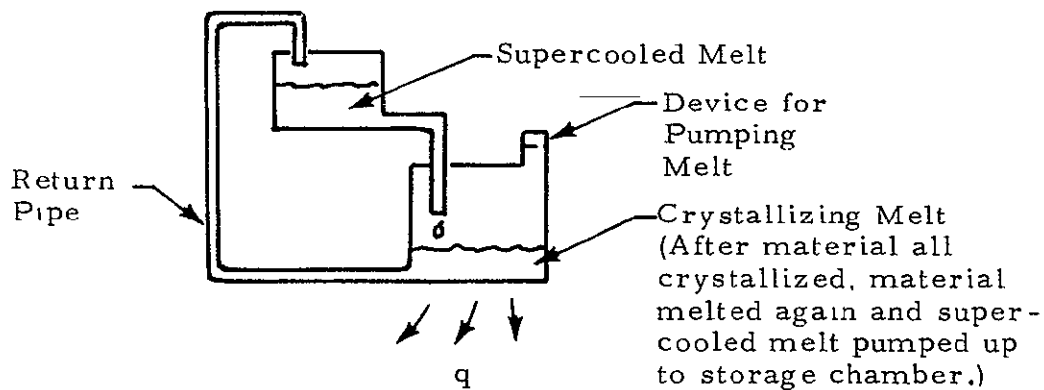

Fig. 6 - Schematic for HS/TC by Supercooled Melts

2.3 GENERAL REMARKS

The A and B type storage modes each possess their own particular characteristics which may be particularly advantageous for certain applications. The advantages of type A are obviously that heat storage is very efficient. Essentially all of the heat input (minus heat leaks) can be stored. On the other hand, good insulation or large amounts of storage material may be required. In the case of type B, the storage of heat may not be as efficient as in type A but could have the advantage of less system bulk, especially if, as implied in Fig. 3, one of the material components can be vented to or admitted from outside the system. Also, a greater option exists in the B type storages for control on collection, storage, and delivery temperature. Section 4 discusses the question of efficiencies in each type storage in more detail.

Section 3
SELECTION OF HS/TC MATERIAL CANDIDATES

In this section, specific HS/TC material candidates are given along with a rating of 1 or 2. A rating of 1 means the material is definitely a candidate for further investigation, and 2 the material appears interesting but further data are required. It might be added that the task of locating chemical reaction candidates is rather formidable at present because literally thousands of chemical reactions are possible in every temperature range and very little data exist on reversibility and reaction heats or heats of formation. Obviously some guidelines must be developed for selecting likely candidates. Probably the best course at present is to simply "plunge in" and investigate some reasonably appearing reactions and see what further course of action appears warranted. In the remainder of the study, some experimental investigations will be conducted of some of the 1 rated candidates and also on some selected 2 rated candidates.

As indicated in the introduction the focus of the study is on storage in the high and low temperature ranges, with particular emphasis on the low temperature range. In the course of searching for candidates in the low and high temperature ranges, however, a couple of interesting candidates in the medium temperature range were uncovered. The medium range candidates are included here because of the present interest in this range for solar home heating/cooling applications. The data on material candidates are presented according to temperature regime and to storage principle. The letters A or B in parentheses indicates likely storage type as indicated in the previous discussion.

3.1 LOW TEMPERATURE RANGE (< 0°C)

Sensible Heat Candidates (A)

As indicated in the previous discussion it is hard to find materials that have heat capacities greater than about 4.185 joules/gm°C). In the low temperature range, however, four materials have been located that possess unusually high specific heats. Unsurprisingly one is water. The other three are ammonia and the mono- and dihydrates of ammonia. These are rated materials along with a candidate in the two category are given in Table 1. One of the candidates given in Table 1, $2NH_3 \cdot H_2O$, incidentally displays a second order phase transition, as shown in Fig. 7.

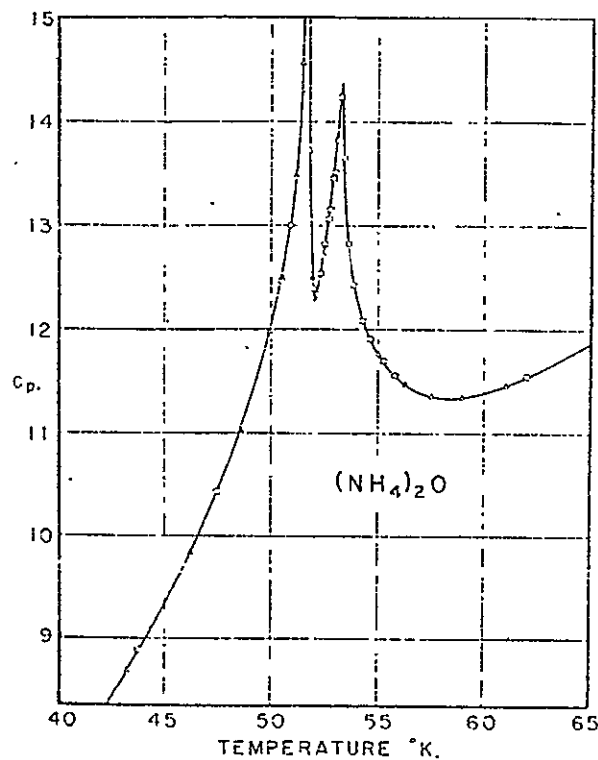Fig. 7 - Anomaly in Heat Capacity of $2NH_3 \cdot H_2O$ or $(NH_4)_2O$; C_p in cal/mole^{-1}/ deg^{-1} (Ref. 13)

Table 1

LOW TEMPERATURE SENSIBLE HEAT HS/TC CANDIDATES AND POTENTIAL CANDIDATES

Material	Melting Point (^{o}C)	Boiling Point (^{o}C)	Temperature Range of Specific Heat Values	Specific Heat Joules/^{o}C-gm (cal/^{o}C gm) (C_p)	Reference	Rating
Water (H_2O	0	100			11 .	1
Ammonia (NH_3)	-77.7	-33.35	-103 to -188 (s) -60 (ℓ)	2.10 (0.502) 4.38 (1.047)	11	1
$NH_3 \cdot 2H_2O^*$	-97	~100	-97 to -258 (Solid)	1.93 - 0.04 (0.46 - 0.01)	12	1
			27 to -97 (Liquid)	4.27 - 2.93 (1.02 - 0.70)		
$NH_3 \cdot H_2O^*$	-79		-25.8 to -79 (Solid)	0.04 - 2.59 (0.01 - 0.62)	13	1
			-79 to 17 (Liquid)	3.14 - 4.02 (0.75 - 0.96)		
$2NH_3 \cdot H_2O^*$	-78.8		-259 to -86.22 (Solid)	0.08 - 2.30 (0.02 - 0.55)	13	1
			-76 to 0 (Liquid)	3.81 - 4.35 (0.91 - 1.04)		
$H_2SO_4 \cdot 2H_2O$	-39.51				14	2

*In this series of ammonia-water compounds eutectic formation is possible. The phase diagram, therefore, needs to be investigated.

Reversible Phase Change (A)

An earlier search of the literature for phase change materials (PCMs) in the low temperature range (173 to $273^{\circ}K$) recommends the four candidates given in Table 2. Although the heat of fusion of the ammonia hydrates are a bit lower than the candidate given in the previous study, it is expected that factors such as the larger sensible heats, higher thermal conductivities, and handling ease will tip the scales toward the hydrates. All of the preceding candidates, however, are rated one for the moment. Two rated candidates include those listed in Table 3.

Table 2

LOW TEMPERATURE PCM CANDIDATES (1 RATING)

Material	Melting Point ($^{\circ}K$)	Heat of Fusion Joules/gm (cal/gm)
Dodecane*	263	215 (51.3) (Ref. 15)
Heptanone-4*	240	> 209 (> 50) (Ref. 15)
Tricaproin*	213	> 209 (> 50) (Ref. 15)
Ammonia*	195	333 (80) (Ref. 15)
The present study would add the following:		
$2NH_3 \cdot H_2O$	194	188 (45) (Ref. 13)
$NH_3 \cdot H_2O$	194	171 (41) (Ref. 13)
$NH_3 \cdot 2H_2O$	176	130 (31) (Ref. 12)

*Candidates recommended in prior study.

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Table 3

POTENTIAL LOW TEMPERATURE PCM CANDIDATES (2 RATING)

	Melting Point ($^{\circ}$C)	Boiling Point ($^{\circ}$C)
$H_2SO_4 \cdot H_2O$	-39.51	
Acetone Hydrate	-35	
$B_2H_5 Br$	-104	~10
$Si_3 H_8$	-117.4	52.9
$Si_4 H_{10}$	-93.5	80
COS	-138	-48
$(Si H_3)_2 O$	-144	-15.2
$(Si H_3)_3 N$	-105.6	52
CS_2	-108.6	46.3

Reversible Chemical/Physical Reactions (A)

The reactions selected as candidates are given in Table 4.

Table 4

REVERSIBLE CHEMICAL/PHYSICAL REACTION CANDIDATES
AND POTENTIAL CANDIDATES

(1 Rating)

$2NH_3 \cdot H_2O$ (s) $\rightleftharpoons NH_3 \cdot H_2O$ (s) $+ NH_3$ (g)

$\Delta H_{187.4^{\circ}K}$ = 7532 cal/mole $NH_3 \cdot H_2O$ formed (Ref. 13)

$2NH_3 \cdot H_2O$ (ℓ) $\rightleftharpoons NH_3 \cdot H_2O$ (ℓ) $+ NH_3$ (g)

$\Delta H_{0^{\circ}C}$ = 5863 cal/mole $NH_3 \cdot H_2O$ formed (Ref. 13)

(2 Rating)

$NH_4 NO_3$ (s) $+ NH_3$ (ℓ) $\rightleftharpoons NH_4 NO_3$ (NH_3 solution) (Ref. 16)

$5/4 S_8$ (s) $+ 16 NH_3$ (ℓ) $\rightleftharpoons N_4 S_4$ (sol.) $+ 6(NH_4)_2 S$ (sol.) (Ref. 16)

Irreversible PCM and Chemical/Physical Reactions (B1)

The materials given in these categories but with the A designation would also be candidates for B1 type storage. Steps, however, would have to be taken to ensure that the backward reaction could be controlled. In the case of the chemical/physical reactions this could easily be accomplished in those reactions which liberate ammonia gas. The ammonia gas could be separated from the reacting mixture and reintroduced when heat liberation is required.

3.2 MEDIUM TEMPERATURE RANGE (0 TO 100°C)

Concepts based on sensible and phase change have been and are being dealt with extensively already. Only reversible and irreversible chemical/physical reactions, therefore, will be considered in this temperature range. Both of the systems described are given a one rating.

Reversible Chemical/Physical Reactions (A)

The following one rated candidates have been identified:

● N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g)
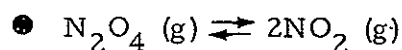
This system, originally suggested by Farrington Daniels (Ref. 17), is quite remarkable in the amount of heat it can absorb from $-11.2°C$ to about $100°C$. The responsible mechanisms are as shown in Table 5.

Table 5

PROPERTIES OF $N_2O_4 \rightleftharpoons 2NO_2$ SYSTEM (REF. 18)

	Temp. (°C)	Heat joules/gm (cal/gm)
N_2O_4 (s) $\rightleftharpoons N_2O_4$ (ℓ)	-11.2	159 (38)
N_2O_4 (ℓ) $\rightleftharpoons N_2O_4$ (g)	21.2	414 (99)
N_2O_4 (g) $\rightleftharpoons 2NO_2$ (g)	20 - 140	632 (~151)

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To the preceding heats must be added, of course, the sensible heats. The various specific heats of NO_2 and N_2O_4 are as follows (Ref. 18):

| | C_p | | Temperature |
	joules/gm-$^\circ$C	(cal/gm-$^\circ$C)	($^\circ$C)
N_2O_4 (s)			
(ℓ)	1.51	(0.36)	-10 to +20
(g)			
NO_2 (g)	0.81	(0.193)	25

As indicated previously, reversible reactions such as the one under discussion have the effect of increasing effective specific heat. For example, the heat capacity of an equilibrium mixture of N_2O_4 and NO_2 as a function of temperature is generally as shown in Fig. 8. It can be seen that the operation of the chemical equilibrium gives the system a heat capacity of about twice that of water (~4.185 joules/gm-$^\circ$C). The preceding is on a weight basis and the N_2O_4/NO_2 system is gaseous. Therefore, the system probably would not be too practical for storage purposes at atmospheric pressure. It would, however, be interesting to see if higher pressures could circumvent this disadvantage. With regard to higher pressures, it is interesting to note that the peak of the curve shifts to higher temperatures as pressure increases. This could be a decided advantage for storage purposes. Also the large heat capacity of the system would present advantages for a heat transfer medium, if not as a storage medium. Another disadvantage of the system is the corrosive nature of the gases. Safety and handling procedures for this system, however, are well documented (Ref. 18).

Irreversible Chemical/Physical Reactions (B2)

It is possible to separate components of a solution by thermal diffusion (Clusius-Dickel technique) as discussed previously. During the course of a previous study (Ref. 10) it was demonstrated that aqueous salt solutions could be separated fairly rapidly with packed columns in the medium temperature
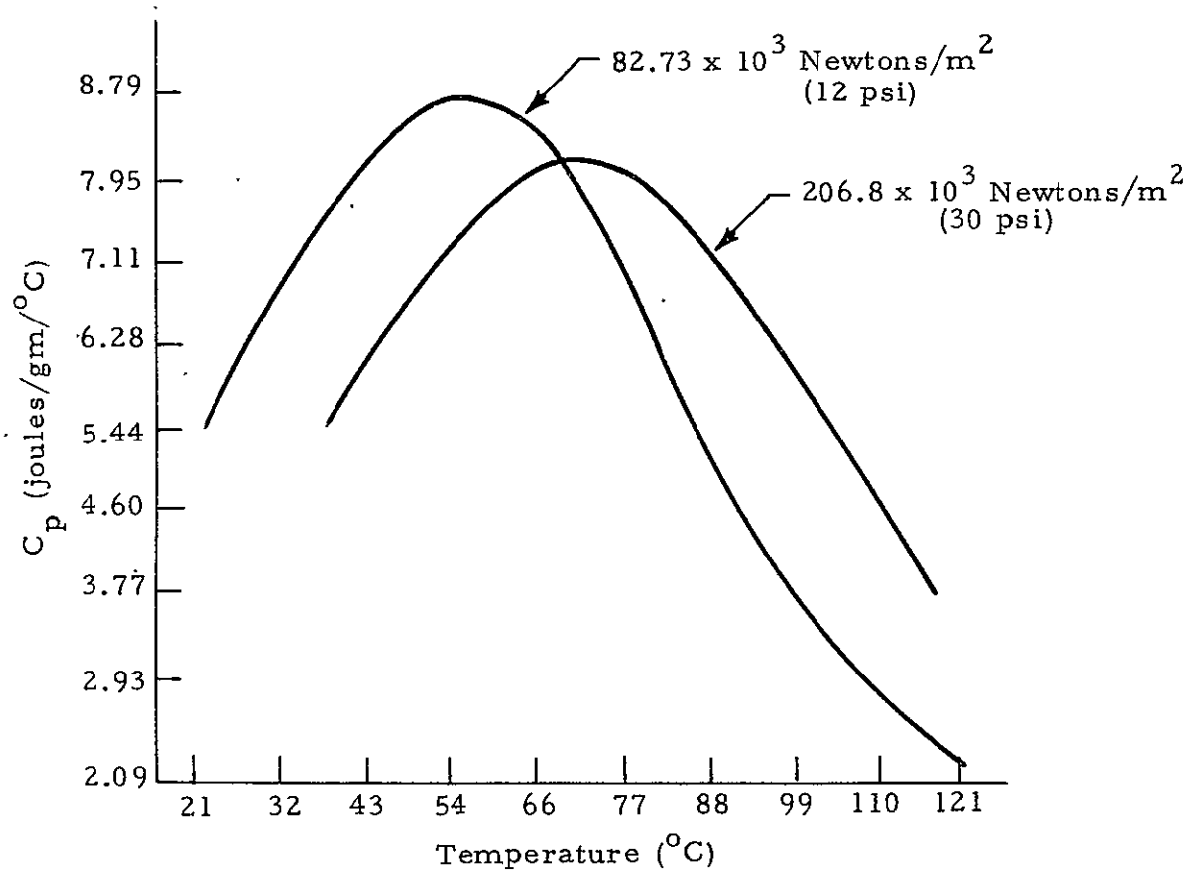
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Fig. 8 - Heat Capacity of $N_2O_4 \rightleftharpoons NO_2$ Mixture (Ref. 18, p. 99)

range. It will be of interest therefore to see what separations of sulfuric acid or other electrolytes might be achieved in this manner. The heat of solution of sulfuric acid in a large amount of water is 80 k joules (19.0 kcal).

3.3 HIGH TEMPERATURE RANGE (> 100°C)

Combined Sensible Heat and PCM Candidates (A)

A number of previous studies have identified or used PCMs in the very high temperature region. These are:

| Material	Melting Point (°C)	Heat of Fusion joules/gm (cal/gm)	Ref.
LiO_2	1427	1967 (470)	19
LiF	848	1046 (250)	19, 20
MgF_2	1263	937 (224)	19
LiH	680	2616 (625)	21, 22
$LiF/Mg\ F_2$	746	774 (185)	23
$Li_2O \cdot B_2O_3$	760	720 (172)	24, 25
3BeO-2MgO	1875	1548 (370)	26
$12\ NaF/40KF/44LiF/4MgF_2$	450	699 (167)	27

The preceding are, of course, in the very high temperature range. This range is of interest for space power applications and for earth solar energy conversion applications. PCMs are also sought in the 93 to 100°C range for use with solar powered heating/air conditioning devices (Ref. 28). As of yet no suitable PCM has been found for this application. The main drawback of any candidate so far has been the PCM cost. One possibility may be molted salt eutectics. For example:

	Melting Point (°C)	Heat of Fusion joules/gm (cal/gm)
$44NaCl + 56\ FeCl_3$	158	218 (52)

The melting point of the example is a little too high for the indicated application. The example, however, is indicative of the possibilities.

Reversible Chemical/Physical Reactions (A)

A previous study surveyed the chemical literature for suitable reactions in the very high temperature range (Ref. 24) The results of the search were disappointing with regard to the study objective which has to find HS/TC materials for spare power applications. The main problem was that no high reaction heat reactions could be found that did not involve a gas phase. The study, however, is instructive, pointing out as it does the involved kinetics at high temperatures. For example, in the reaction

$$Li \ C\ell + Ca$$
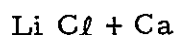
the following species and equilibria are involved:

Species: $LiC\ell$ (ℓ), $LiC\ell$ (g), Ca (ℓ), Ca (g), $CaC\ell_2$ (ℓ), $CaC\ell$ (g), $C\ell_2$ (g), Li (ℓ), Li (g), Li_2 (g), $C\ell$ (g)

Equilibria:

1. $2 \ LiC\ell$ (ℓ) $+ Ca$ (ℓ) $\rightleftharpoons CaC\ell$ (ℓ) $+ 2 \ Li$ (ℓ)
2. $LiC\ell$ (ℓ) $\rightleftharpoons LiC\ell$ (g)
3. Ca (ℓ) $\rightleftharpoons Ca$ (g)
4. $CaC\ell_2$ (ℓ) $\rightleftharpoons CaC\ell$ (g) $+ \frac{1}{2} C\ell_2$ (g)
5. Li (ℓ) $\rightleftharpoons Li$ (g)
6. $2 \ Li$ (g) $\rightleftharpoons Li_2$ (g)
7. $LiC\ell$ (g) $\rightleftharpoons Li$ (g) $+ \frac{1}{2} C\ell_2$ (g)
8. $CaC\ell$ (g) $\rightleftharpoons Ca$ (g) $+ \frac{1}{2} C\ell_2$ (g)
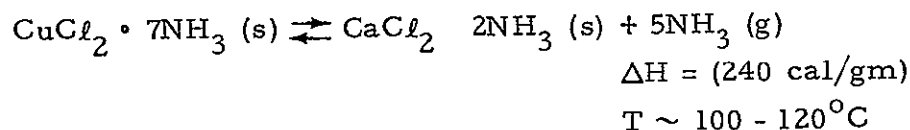9. $C\ell_2$ (g) $\rightleftharpoons 2 \ C\ell$ (g)

Conducting a thermodynamic analysis which included simplifying assumptions, however, the estimate was made in the cited, prior study that the system could store 2325 joules/gm (556 cal/gm) between $1427^{\circ}C$ and $527^{\circ}C$.

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The present author tends to agree with the conclusion of the previous study that it is probably futile to even consider gas phase reversible reaction at extreme high temperatures for storage purposees. This area, therfore, is given no rating at all.
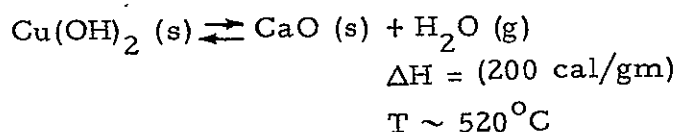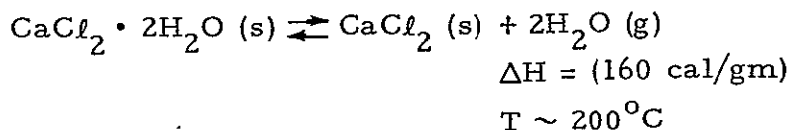
One area, that has not been explored as yet, however, is that of reactions in molten or fused salt solutions. This area is, therefore, given a 2 rating.

Irreversible Chemical/Physical Reactions (B1)

In this category might be listed the following types of reactions:

$$CuCl_2 \cdot 7NH_3 \text{ (s)} \rightleftharpoons CaCl_2 \quad 2NH_3 \text{ (s)} + 5NH_3 \text{ (g)}$$
$$\Delta H = (240 \text{ cal/gm})$$
$$T \sim 100 - 120^\circ C$$

and

$$CaCl_2 \cdot 2H_2O \text{ (s)} \rightleftharpoons CaCl_2 \text{ (s)} + 2H_2O \text{ (g)}$$
$$\Delta H = (160 \text{ cal/gm})$$
$$T \sim 200^\circ C$$

$$Cu(OH)_2 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + H_2O \text{ (g)}$$
$$\Delta H = (200 \text{ cal/gm})$$
$$T \sim 520^\circ C$$

The reactions are rendered irreversible by removal of the gaseous phase. Reactions such as the preceding have been suggested previously by that sage of solar energy utilization — Farrington Daniels (Ref. 17). A current study is exploring both the CaO and MgO systems (Ref. 29). Use of systems such as the preceeding for home heating and crop drying were also discussed by the author at a recent meeting (Ref. 30, attached to this report). The reactions appear so promising that they are all rated one. It might be added that those involving water are particularly advantageous for earth uses because the water vapor can be vented to the environment, thereby avoiding the problem of what to do with a large volume of gas.

A gaseous system called SOLCHEM and employing the following cycle;

$$SO_3 \xrightarrow{\ 800^\circ C\ } SO_2 + \frac{1}{2} O_2$$

450 - 600°C   heat abstracting on cooling

$$SO_2 + \frac{1}{2} O_2$$

storage at 110°C
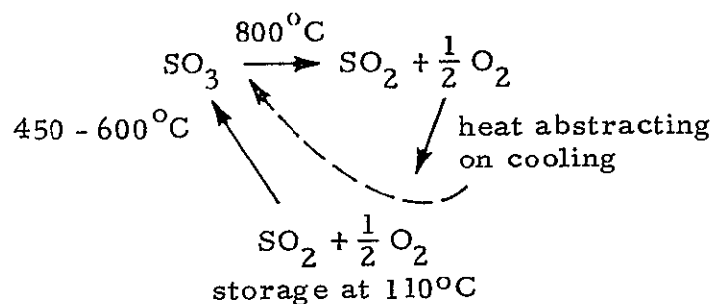
has been recently reported (Ref. 31). The combination of SO_2 and O_2 liberates some 96 kjoules/mole (23 kcal/mole) (Ref. 32). Other reactions obviously are also possible (Ref. 32), but again the objection of what to do with large amounts of gases becomes a problem. So again we would judge the concept as probably promising for collection or heat transfer, but not promising for storage.

The interesting case of water decomposition and storage of the products O_2 and H_2 will be considered in the remainder of the study.

Section 4

THEORETICAL CONSIDERATIONS REGARDING ENERGY STORAGE AND THERMAL CONTROL

As indicated in Section 1, a theoretical framework which would allow various storage and control concepts to be evaluated is generally lacking. Such a framework will, of course, take more time and effort than can be spent in a study of the present kind. However, the survey of concepts presented in Section 2 brought to light some considerations and questions which should be included in any general theoretical scheme. These are outlined in the following discussion. It should be mentioned, incidentally, that only thermal energy storage is considered. Photon energy storage and conversion is not considered.

One of the first questions that immediately comes to mind is: "How many ways can one store energy"? This question is readily answered by consulting the general energy equation

$$dE = TdS - PdV + \mu\,dn + \sigma dA + EdQ + HdM + gmdh - \tau\ell^2 dL$$

where the terms for a closed system, i.e., no addition or subtraction of matter from the system, are identified as follows

TdS	thermal energy
PdV	work to alter volume of system
$\mu\,dn$	chemical energy
σdA	work to extend surface
EdQ	work to electrify system
HdM	work to magnetize a system
gmh	work to increase gravitational potential
$\tau\ell^2 dL$	work to extend elastic system

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As indicated previously, however, it would appear that storage modes other than heat and chemical energy, and possibly electrical energy offer little, if any, advantage. The next question to be answered is how efficient is the storage, i.e., how much of the input heat is redeliverable at will? We are interested for the moment only in storing heat. We, therefore, will address here only the question of what happens to a system if heat is added or subtracted and not what happens to the system if external work is done on or done by the system. In other words we consider here systems as shown in Figs. 9a and not as shown in 9c and 9d.

a. System stores all of heat input q_{in} = q_{out} Batch Situation

b. System stores part of heat input $q_{in} > q_{out}$ Steady State Situation

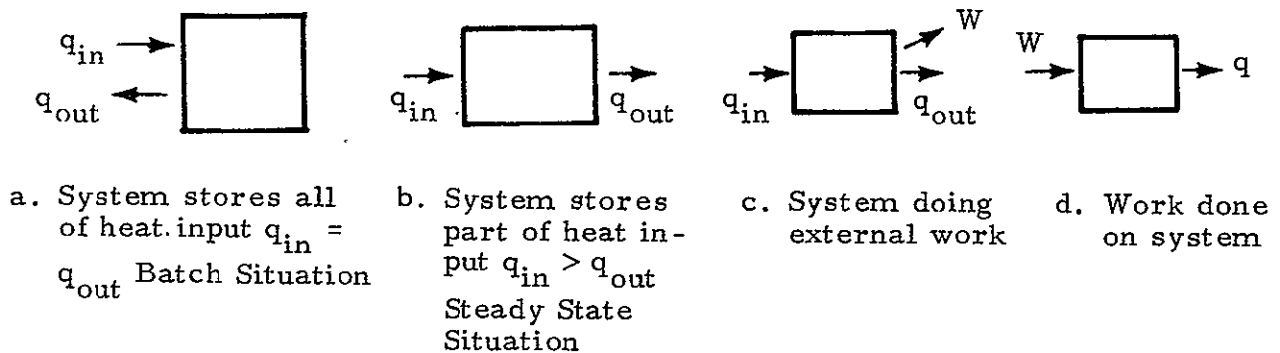c. System doing external work

d. Work done on system

Fig. 9 - Schematics of Various Heat-Work Addition Possibilities

Figure 9a would appear to represent essentially all of A type storage and Fig. 7b B type storage.

As indicated previously, A type storage is essentially 100% efficient if heat leaks can be avoided. The efficiency of A type storage, therefore, need not concern us further here.

B1 type storage would appear to have efficiencies ranging from quite efficient to very low depending on the particlar circumstances. Take for example the case of supercooled melts. The heat input consists of the following:

$$q_{in} = q_{C_p} + q_L$$

where q_{C_p} is the sensible heat required to heat the material to its melting

point and q_L the latent heat of phase change. On cooling to storage tempera-

ture essentially q_{C_p} is lost. Thus the storage efficiency is essentially

$$E_S = \frac{q_L - q_{C_p}}{q_L + q_{C_p}}.$$

Supercooled melts, therefore, may be fairly efficient or fairly inefficient de-

pending on the relative magnitudes of q_L and q_{C_p}.

· The question of efficiency appears to be more complicated in B2 type

storage i.e., Fig. 9b and Figs. 3, 4 and 5. In B2 type storage a flow of heat

from T_2 to T_1 must necessarily be maintained during the storage operation,

for example, see Figs. 3 and 4. Thus we have in effects a Carnot cycle in

which internal work is being performed. The limiting efficiency of such a

process would therefore be given by:

$$\frac{q_{stored}}{q_{in}} = \frac{T_2 - T_1}{T_2}$$

assuming of course that a mechanism exists that would be 100% effective in

converting available energy into potential energy.

The next question is the magnitude of actual or realistic efficiencies.

These would appear to be governed by the availability of a suitable mechanism

for performing work and the rates of heat input and work performance. Con-

sider, for example, the case of separation by thermal diffusion. A system such

as pictured in Fig. 4 is in a semi-steady-state (SSS) condition. That is to say

heat transport by thermal conduction is essentially at steady state (SS). Sepa-

rative work, however, is being performed. Separative work would continue

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to be performed until the rate of separation by thermal diffusion became equal to the rate of back diffusion by ordinary chemical diffusion or until steady state. Onsager worked out a relationship for maximum, actual efficiency of a thermal diffusion separation. This can be given by the following ratio (Onsager gave the ratio in terms of entropy increases and decreases):

$$E_o = \frac{\text{maximum rate of work performance}}{\text{rate of heat transport by conduction}}$$

The condition of maximum work performance according to Onsager is when

$$J_{TD} = 2\, J_D$$

that is, when the mass flux due to thermal diffusion is twice the back mass flux due to ordinary diffusion. Further discussion of the Onsager efficiency is given in Ref. 10.

If the preceding line of reasoning remains valid after a more thorough study, the practical limits on storage efficiency can be identified as the activation energy barriers to rate processes such as ordinary diffusion, thermal diffusion, electrodiffusion, magnetodiffusion, and so on. Also, it is fairly obvious that each heat storage mode will necessarily be limited as to the amount of heat storage. For example, if the heat flux to a system performing work by thermal diffusion is exceeded, i.e., if the heat is supplied faster than can be transported or absorbed by conduction and thermal diffusion, boiling will then set in.

The preceding theoretical concepts need, of course, to be further studied and validated. In the remaining portion of the study a little more thought will be given to the theoretical aspects.

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Appendix
SOME PRACTICAL ASPECTS OF THERMAL ENERGY STORAGE

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SOME PRACTICAL ASPECTS OF THERMAL

ENERGY STORAGE

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on

Solar Energy Storage Subsystems

for the Heating and Cooling of Buildings

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Charlottesville, Virginia

# SOME PRACTICAL ASPECTS OF THERMAL ENERGY STORAGE

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Abstract

Problems associated with solar thermal energy storage systems based on materials that store heat either as sensible heat or as latent heat of fusion are reviewed. Energy storage by chemical reactions as a means to circumvent some of the problems noted with sensible or latent heat materials is considered. The consideration identifies a number of potential advantages for materials that store energy by chemical reaction over sensible or latent heat stores. Among the foreseen advantages are larger heat capacitance, simpler and more efficient system designs, and more options with regard to collection and delivery temperatures.

Solar thermal energy storage systems based on materials which store heat, either as sensible heat or as latent heat of fusion possess the general characteristics shown in the following schematic.
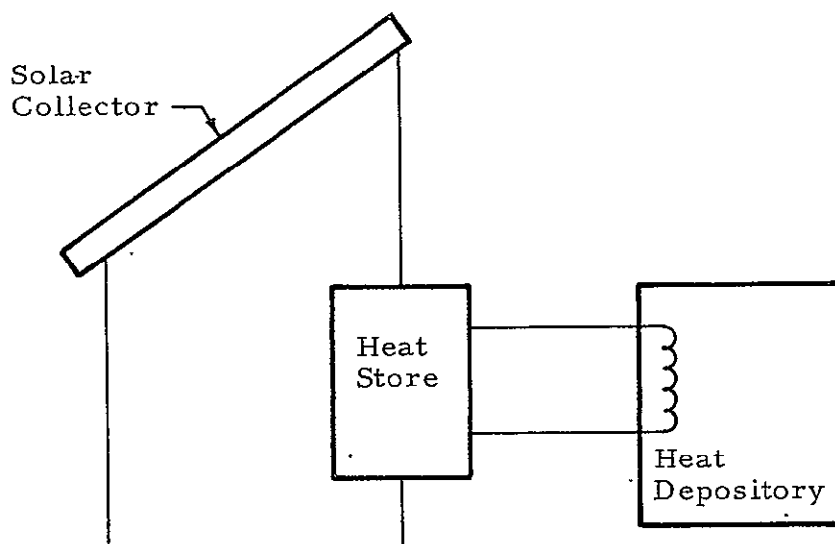
Essentials of Solar Thermal Energy Storage Systems

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A number of problems are associated with actual operation, however. These can be categorized according to the heat storage material used. For convenience of discussion, materials that store heat as sensible heat here are called TCMs, an abbreviation for thermal capacity materials. Those that store heat as latent heat of fusion are usually called PCMs, an abbreviation for phase change materials. The summary of operational problems, according to the heat storage material, is as follows.

TCM

- TCM temperature continuously rises during collection. The result is greater and greater convective heat losses.

- TCM temperature continuously drops during heat deposition. The result is smaller and smaller heat flux deliveries.

- Large quantities of TCMs are required, which may pose installation problems in established homes.

- Because the optimum delivery temperatures are different for heating and cooling requirements, two storage tanks are required for dual function subsystems.

- If water is used as a TCM the highest practical storage or delivery temperature is near $100^{\circ}C$ ($212^{\circ}F$) which poses a problem in that storage for cooling is only between 200 and $212^{\circ}F$.

- Heat storage in TCMs occurs at temperatures higher than ambient. Insulation to prevent heat losses is therefore required which adds to system cost.

PCM

- Because of the nature of PCMs the material itself if not usually used as a heat transfer agent, i.e., separate fluid loops are usually required for heat pickup at the solar collectors and heat delivery at the depository.

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- PCMs typically possess low thermal diffusivities, necessitating special (i.e., expensive) heat exchangers.

- A variety of operational problems is associated with PCM usage. For example, some PCMs "melt" to form a liquid phase and another solid phase. The second solid can sink and thus not be available for the reaction to reform original PCM. Other problems include eventual destruction by repeated thermal cycling of catalyst added to overcome supercooling. Additionally, corrosion of the PCM container can introduce impurities that can affect performance.

- Careful consideration must be given to the design of heat exchangers to ensure that the PCM freezing rates can keep up with the rates of heat removal. Again, special designs may be required which can result in added costs.

- Relatively few inexpensive PCMs have been identified (Ref. 1).

- As with TCMs, two different PCMs and two storage tanks are required for systems that incorporate both heating and cooling subsystems. Dual PCM storage is required because the optimum delivery temperatures are different for heating and cooling.

- PCM heat storage temperatures, if significantly different from ambient, may require specially insulated storage containers.

The preceding discussion is meant to indicate some of the problems that can be encountered with TCMs and PCMs. A number of the problems, if not all, will undoubtedly be resolved satisfactorly in the course of further research and development on TCMs and PCMs. It is appropriate, however, to inquire what the advantages might be of systems based on chemical reactions or CCMs (an abbreviation for chemical change materials).

The concept of utilizing CCMs for energy storage is a relatively new, undeveloped concept at present. The main attraction of CCM systems is that the heats of reaction can be considerably larger than sensible heats and heats of fusion. Farrington Daniels (Ref. 2) mentioned a few CCM possibilities, but to the best of our knowledge only recently has the concept attracted more than cursory attention (Refs. 3, 4 and 5). It is necessary, therefore, at this point, in time to seek to gain some understanding of the operation of chemical reactions with regard to heat storage. A consideration of the operation of PCMs

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is worthwhile in this regard because the principles involved are generally the same as for CCMs. PCM operation furthermore is simpler than CCM and therefore more suitable for orientation purposes. The following is a brief review of PCM operation. More detailed considerations of PCM operation are available in Ref. 6.

Consider the operation of a PCM as a heat storer in the following device:
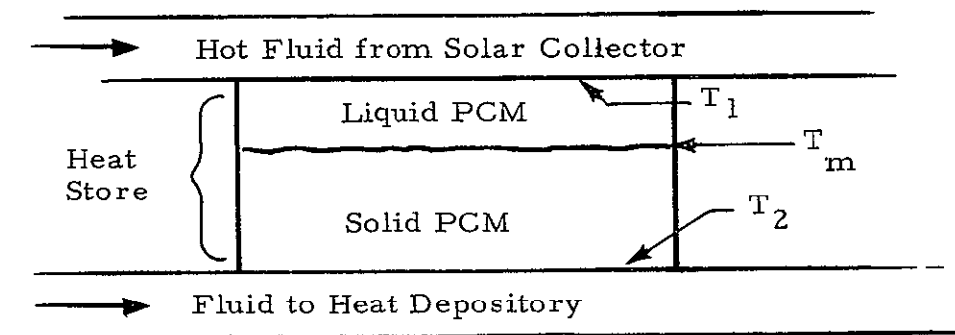
The terms T_1, T_m, and T_2 are temperatures at the indicated locations. The The temperature T_1 needs to be somewhat higher than T_m or the temperature at the solid/liquid interface in order to transfer heat to the melting PCM. The temperature T_2 needs to be somewhat lower than T_m in order to transfer heat from solidifying PCM. If the thermal diffusivities of solid and liquid PCMs are high T_1 and T_2 need not be much greater or lower than T_m. In such a case heat can be collected and delivered by the PCM at essentially the melting temperature of the PCM.

Another arrangement can be conceived: suppose that the liquid as it is formed is siphoned and stored in a separate container. Suppose further that the PCM liquid will not freeze without the adding of a catalyst. The temperature of the liquid PCM can thus be allowed to drop far below the melting point, and heat can be stored in the PCM at ambient temperatures without the need of elaborate insulation. When the need for heat delivery arises the liquid PCM can be inoculated with catalyst. Furthermore, suppose that the super-cooled, liquid PCM is subjected to a pressure higher than that at which it was
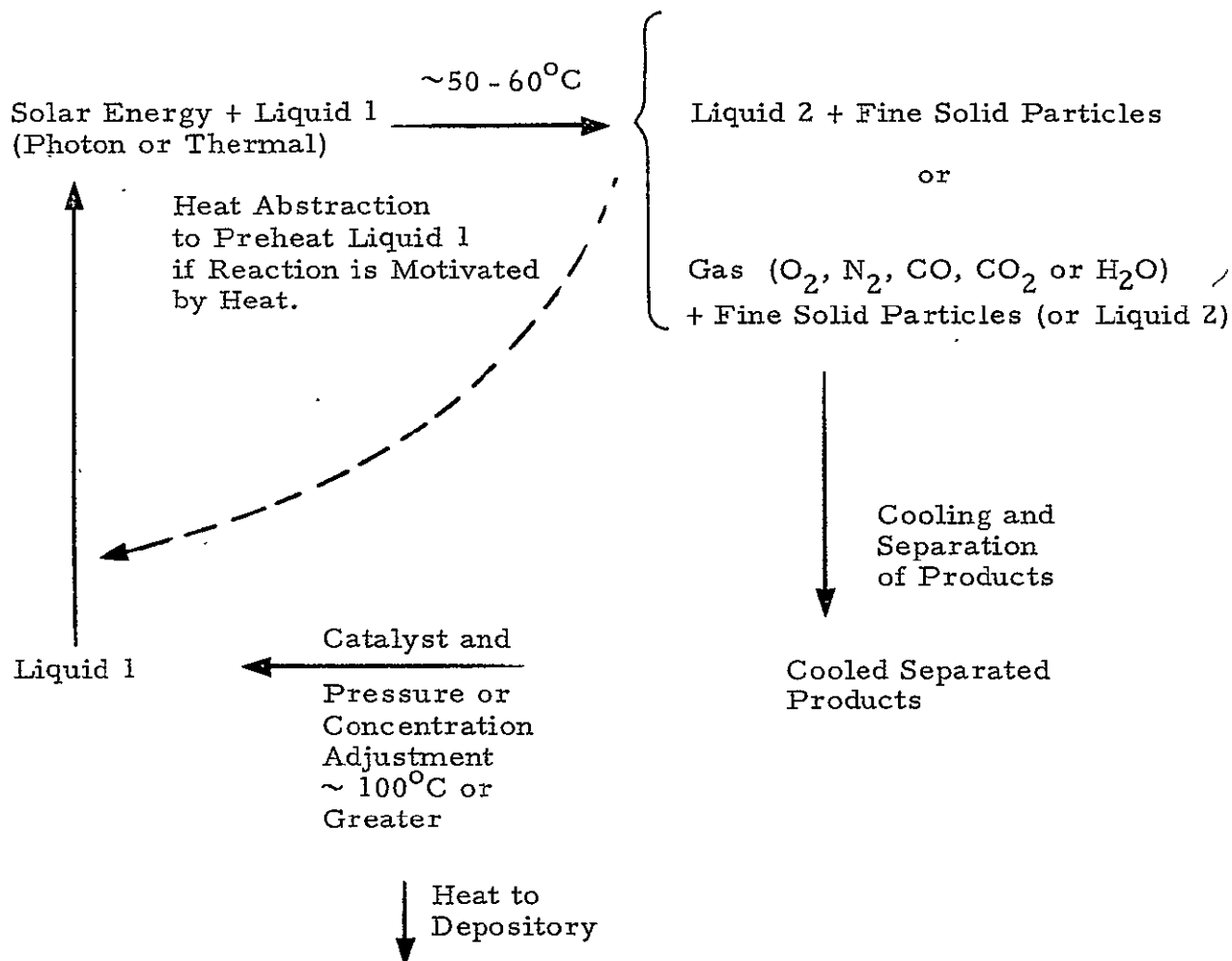
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melted. Most substances possess melting point temperatures that increase as pressure is increased, water being the exception (Ref. 7). By increasing the pressure on a supercooled, liquid PCM, freezing theoretically can occur at a higher temperature than that at which melting occurred. Heat delivery at a temperature higher than that at which heat collection and storage occurred is thereby possible.

To consider now the operation of CCM systems, it is convenient to utilize for orientation purposes the chemical system suggested in Ref. 3 for high temperature solar heat collection and delivery. The system under discussion is called the SOLCHEM system and depends on the following gaseous, chemical cycle.
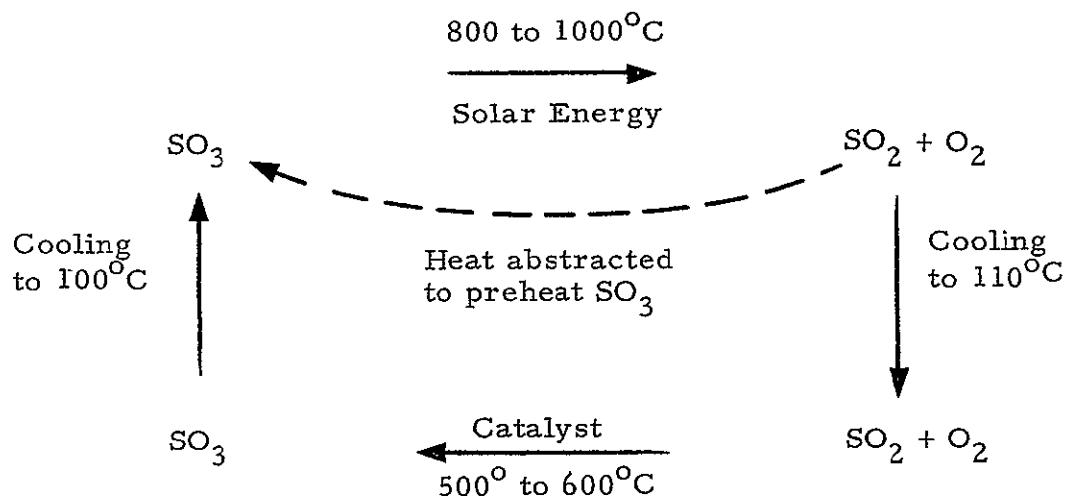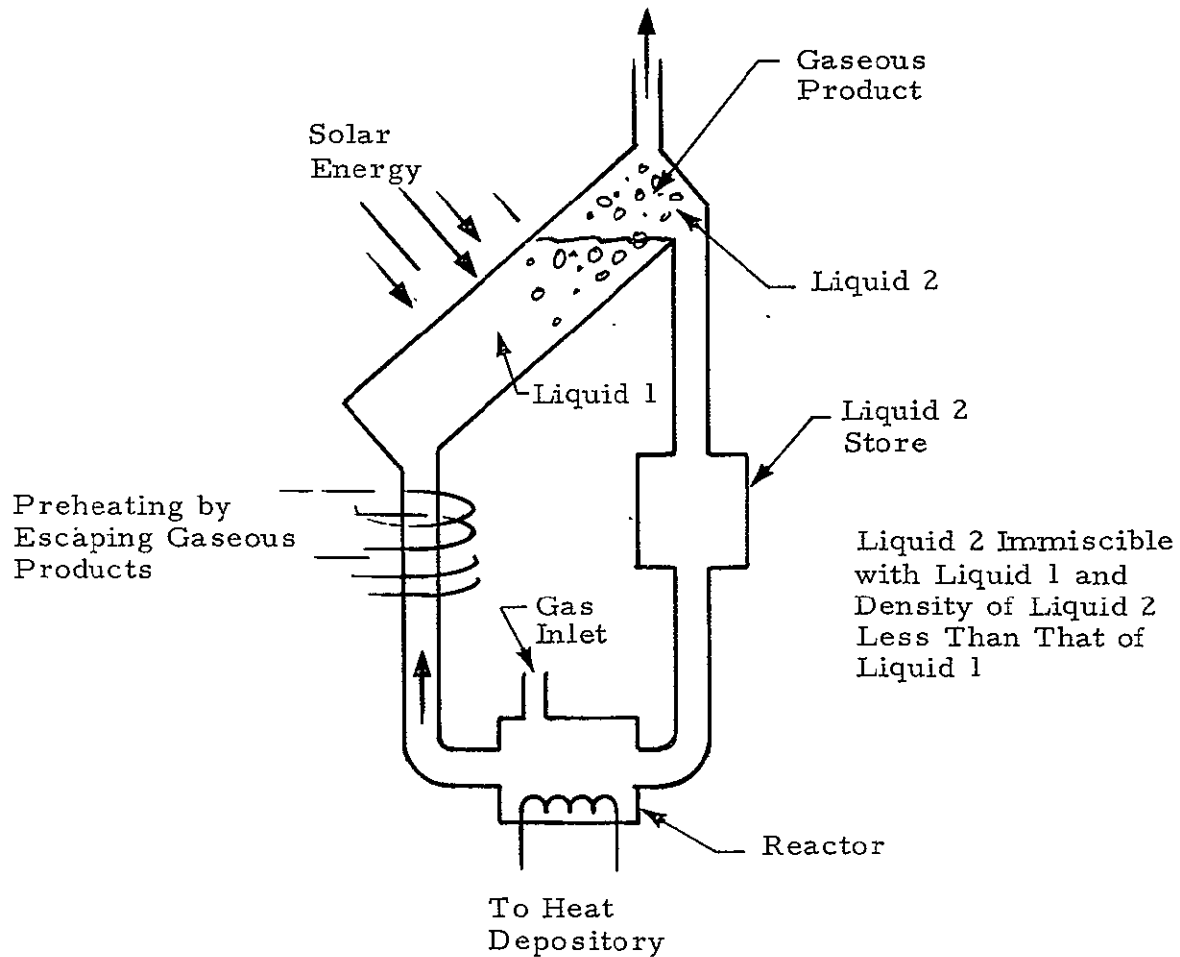

The dissociation of SO_3 into SO_2 and O_2 absorbs heat energy while the recombination of SO_2 and O_2 liberates some 23 kcal/mole (Ref. 3). The SOLCHEM system, it should be noted, does not possess the capability of delivering heat at a temperature higher than that at which it was collected.

With the preceding discussion as background, a conception of desirable characteristics for a CCM system for home heating and cooling may be considered. Some desirable characteristics are indicated in the schematic on the following page.

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Solar Energy + Liquid 1
(Photon or Thermal)

$\sim 50 - 60^{\circ}C$

Liquid 2 + Fine Solid Particles

or

Gas (O_2, N_2, CO, CO_2 or H_2O)
+ Fine Solid Particles (or Liquid 2)

Heat Abstraction
to Preheat Liquid 1
if Reaction is Motivated
by Heat.

Cooling and
Separation
of Products

Liquid 1

Catalyst and

Pressure or
Concentration
Adjustment
$\sim 100^{\circ}C$ or
Greater

Cooled Separated
Products

Heat to
Depository

Desirable Characteristics for a Solar CCM Storage System

A CCM system depending on liquid and solid reactants is viewed as
desirable to minimize storage volumes. Liquids furthermore can be used
as the heat transfer agents. Where gases might be evolved, it is desirable
that they can be obtained from or vented to the atmosphere. The attractive-
ness of having reactions where a liquid is decomposed into another liquid and
solid particles or gas lies in the ease of separation and subsequent storage.
For example, consider the schematic on the following page.

Solar Energy

Gaseous Product

Liquid 2

Liquid 1

Liquid 2 Store

Preheating by Escaping Gaseous Products

Gas Inlet

Liquid 2 Immiscible with Liquid 1 and Density of Liquid 2 Less Than That of Liquid 1

Reactor

To Heat Depository

If solid particles are generated in the chemical reaction they can be separated by sedimentation. The motivating force for the chemical reaction may be either photonic or thermal solar energy, although photon chemical reactions investigated to date have apparently proved to be quite inefficient. The preceding brief discussion should serve to indicated the general considerations relevant to CCM storage systems. A number of specific questions, of course, arise. Two that are anticipated to be of utmost importance are:

- Identifying specific CCMs, and
- Controlling reaction rates either by catalysts, pressure, or reactant concentrations to achieve desirable temperatures.

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The mentioned areas require detailed considerations of factors such as reversibility of any given reaction as a function of temperature and pressure, reaction rate control, catalyst identification and procurement, possible side reactions, materials compatibilities and toxicities, materials and equipment costs, and so on. The incentive for pursuing development of CCM systems lies in their potential advantages which may be summarized as follows:

Theoretical Advantages of CCM Storage Systems for Home Heating/Cooling

- Heat collection and delivery at essentially constant temperatures.

- Delivery temperatures higher than collection temperatures.

- Larger heat storage potential than either TCMs or PCMs.

- Storage at ambient temperatures.

- One storage tank which would meet both heating and cooling requirements.

As mentioned previously some of the stated advantages for CCMs can apply also to PCMs. The potential advantages of CCMs over PCMs lie in their larger heat storage capacities, the ability of CCMs to be both the heat transfer and heat storage media, and the greater number of options offered by CCMs with regard to collection and delivery temperatures and storage arrangements.

It is evident that the CCM storage concept will require an extensive research and development before its practicality can be assessed. Two specific CCM systems can be mentioned which appear interesting at present and which can serve the purpose of model systems for definition of important problem areas. The first involves the following reactions.

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$$N_2O_4 \text{ (gas)} + 147 \text{ cal/gm} \rightleftharpoons 2NO_2 \text{ (gas)}$$
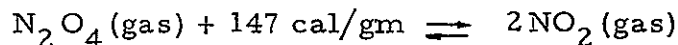
Temperature range = -11.2 to 73°C

$$NO_2 \text{ (gas)} + 151 \text{ cal/gm} \rightleftharpoons NO \text{ (gas)} + 1/2 \, O_2 \text{ (gas)}$$
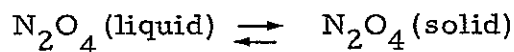
at temperatures over 60°C

Two disadvantages of this system are that it is essentially gaseous and the $N_2O_4 \rightleftharpoons NO_2$ reaction proceeds as readily backward as it does forward without a catalyst. However, it may be possible to retard the back reaction by lowering pressure or by other means which will perhaps become obvious when the kinetics of the reaction are studied in detail. Another possibility that warrants investigation is to conduct the reaction in solution. The N_2O_4-NO_2 system offers further avenues for storing heat. These lie in the rather large heats of fusion and vaporization and are given in the following set of reactions.

$$N_2O_4 \text{ (liquid)} \rightleftharpoons N_2O_4 \text{ (vapor)}$$
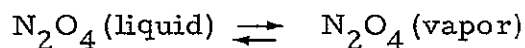
$$\Delta H_v = 198 \text{ cal/gm}$$

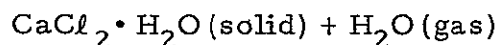$$T_{boiling} = 21.15°C$$

and
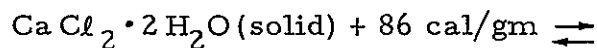
$$N_2O_4 \text{ (liquid)} \rightleftharpoons N_2O_4 \text{ (solid)}$$
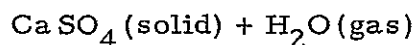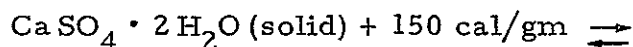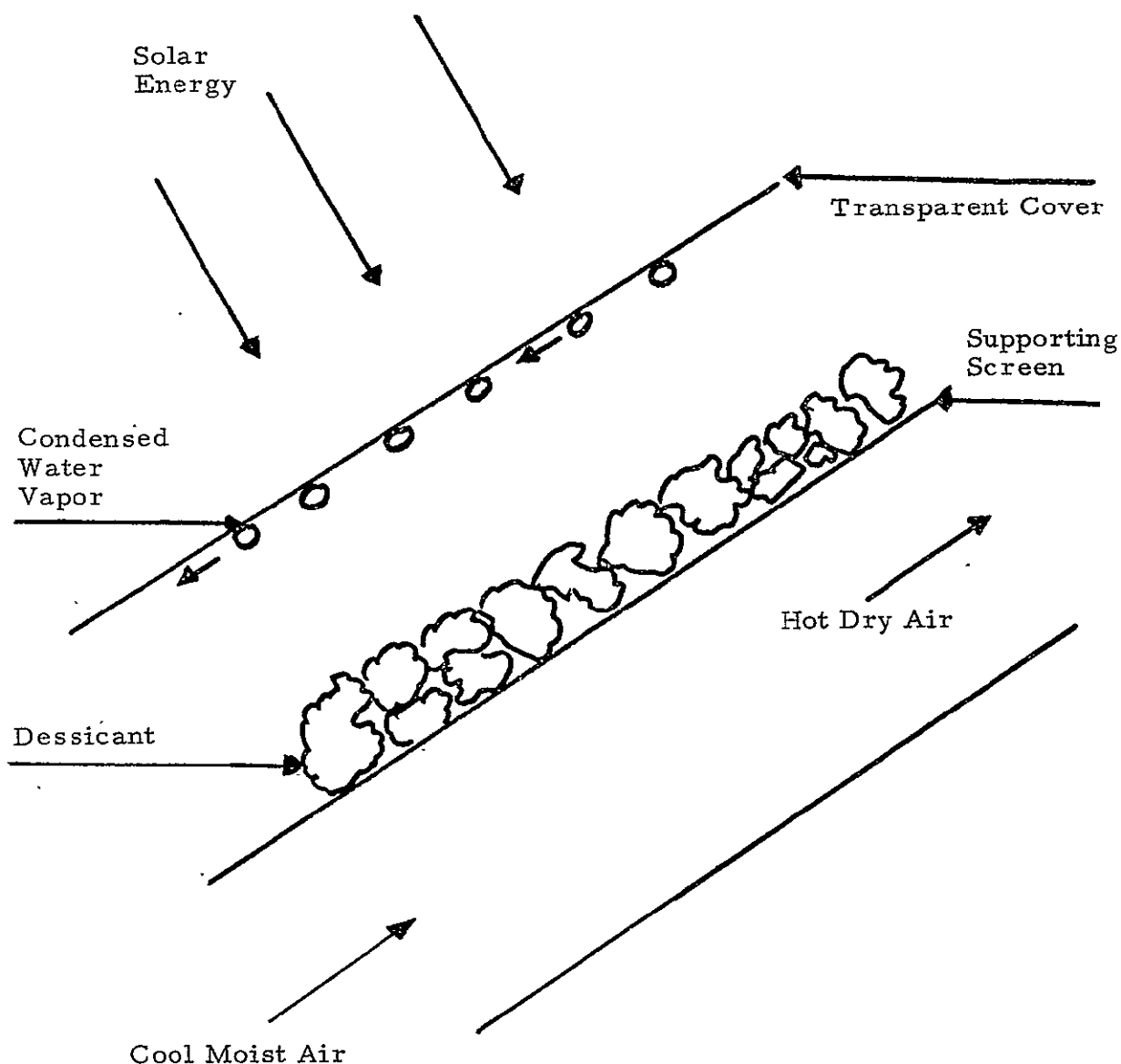
$$\Delta H_f = 76 \text{ cal/gm}$$

$$T_{melt} = -11.2°C$$

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With ingenuity in storage system design it, may be possible to utilize all of the indicated heats. The total would be an approximately 572 cal/gm over a temperature range of $-11.2^{\circ}C$ to about $100^{\circ}C$.

The other chemical system that appears interesting for further investigation is one based on one of the following chemical reactions.

$$CaSO_4 \cdot 2H_2O \text{ (solid)} + 150 \text{ cal/gm} \rightleftharpoons$$

$$CaSO_4 \text{ (solid)} + H_2O \text{ (gas)}$$

$$CaCl_2 \cdot 2H_2O \text{ (solid)} + 86 \text{ cal/gm} \rightleftharpoons$$

$$CaCl_2 \cdot H_2O \text{ (solid)} + H_2O \text{ (gas)}$$

$$Ca(OH)_2 \text{ (solid)} + 200 \text{ cal/gm} \rightleftharpoons$$

$$CaO \text{ (solid)} + H_2O \text{ (liquid)}$$
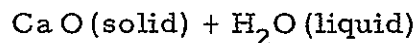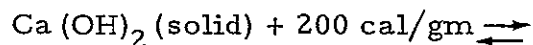
The attractive feature of systems based on these reactions is that one of the products, water, can be vented to or obtained from the atmosphere. Part of the storage volume problem can thereby be circumvented. Another attractive feature is that the indicated dessicants are very cheap. Studies on dessicant use for crop drying purposes are currently being pursued at Lockheed-Huntsville. The concept, however, can be readily adapted for home heating purposes. One conceptual scheme utilizing dessicants for crop drying is indicated in sketch shown on the following page.

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Solar
Energy

Transparent Cover

Supporting
Screen

Condensed
Water
Vapor

Dessicant

Hot Dry Air

Cool Moist Air

Concept for Collector/Storage System for Crop Drying

Conclusions

Energy storage systems based on chemical reactions promise a number of attractive advantages over TCMs or PCMs for home/heating cooling applications. The CCM concept for home heating and cooling applications, however, is an untried concept. Preliminary information and studies performed to date, however, indicate the CCM concept feasible and worthy of further research and development.

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